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THE DETERMINATION OF CADMIUM  
IN ZINC CONCENTRATES

BY

LYNN ANDRE WATT

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THESIS FOR THE DEGREE OF BACHELOR OF SCIENCE

IN CHEMISTRY

IN THE

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

*Sydney A. Watt.*

ENTITLED *The Determination of Cadmium*  
*in Zinc Concentrates.*

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF *Bachelor of Science.*  
*in Chemistry.*

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## The Determination of Cadmium in Zinc Concentrates.

The chief source of cadmium is the ore of other metals, especially zinc blende, where it exists merely as an impurity. Present as the sulphide it is the chief constituent of one ore, greenockite, which is found in relatively small amounts in Scotland, Bohemia, and Pennsylvania. The amount of cadmium which is contained in zinc blende varies greatly with the locality from which the ore is obtained. As a rule, however, the range is somewhere between one-tenth and five-tenths of one per cent.

When the zinc blende which contains cadmium sulphide is roasted, some of the latter is converted to the sulphate. This resists heat tolerably well and may be dissolved out of the roasted blende with water. When distilled with charcoal, however, most of the cadmium distills over before the zinc. This may be noticed very readily as the cadmium burns at the nose of the condenser giving a characteristic brown color to the flame.

As already mentioned the amount of cadmium present in zinc blende is usually only a very few tenths of one per cent. It would seem that its presence in such a small quantity would be negligible under ordinary circumstances. In a measure this is entirely true, yet of late years the managers of the smelters have asked for a



determination of the cadmium content. No doubt their reason for doing so has originated from complaints by the trade.

It is easily understood why zinc white, even though it contains but a very small amount of cadmium, should develop a yellowish tinge after considerable exposure to the atmosphere. This should be especially noticeable in cities, where the coal smoke carries an increased amount of hydrogen sulphide. Besides this objection, the cadmium is said to give brittleness to the metallic zinc.

It is the accurate determination of this relatively minute quantity of cadmium as it exists in the zinc concentrate, which has given the assayers and analysts not a little trouble. The object of the present investigation is to devise a method for its determination, which may have the required accuracy and at the same time a proper degree of rapidity. Obviously this end may be accomplished either by the adaptation of some method already in existence, or by developing an entirely new one.

In going through the literature it became evident very soon that there were few references of any value on the subject. There are several methods which may be used for the determination of cadmium, but its separation from zinc and other metals, is restricted almost entirely to its precipitation as the sulphide in either acid or cyanide solutions. All of the methods for separation,





however, pre-suppose the existence of the cadmium in relatively large amounts.

The method of repeated precipitation as the sulphide in about a five per cent solution of sulphuric acid has found considerable favor among the assayers of the Joplin district. The successive precipitates of cadmium sulphide are dissolved by heating gently with dilute hydrochloric acid ( 1-10 ). After the final precipitation the sulphide is converted to the sulphate, heated very carefully to a dull red, and weighed.

Another method is that suggested by Fox, who precipitated the cadmium as the sulphide in a solution containing trichlor-acetic acid. When the amount of zinc was considerably larger than that of the cadmium the separation was not complete. On dissolving the cadmium sulphide and reprecipitating, however, very good results were obtained.

The precipitation of the sulphide in a solution containing potassium cyanide is a method which has been often used in the determination of cadmium. This method, which is due to Wohler, gives a very complete separation of cadmium from any copper which may be present.

Another method involving the use of potassium cyanide is that suggested by Low. Instead of precipitating the cadmium in a cyanide solution, he advises the ordinary precipitation in a four or a six per cent solution of sulphuric acid. The precipitate consisting of the mixed



sulphides of cadmium, copper, and possibly lead and bismuth, with a small amount of zinc, is filtered off and washed several times with water containing hydrogen sulphide. Then the beaker in which the precipitation took place is set under the funnel and a small amount of a very concentrated solution of potassium cyanide is poured upon the filter. Only enough cyanide is used to dissolve the zinc and copper sulphides. The solution now in the beaker is once more poured through the filter, whereupon, if lead and bismuth are absent, a pure yellow or orange colored precipitate of cadmium sulphide should remain. Should the precipitate still be dark it may be boiled with dilute hydrochloric acid, thus dissolving the sulphide of cadmium entirely. The resulting solution is then just neutralized with sodium carbonate, the lead or bismuth filtered off, the cadmium reprecipitated as the sulphide, converted to the sulphate and weighed.

In determining the cadmium after it has been isolated it may be precipitated from a boiling solution with either potassium or sodium carbonate. The former is to be preferred, however, since it admits of a more thorough washing of the precipitate. After standing on the water bath until the precipitate has settled the cadmium carbonate is filtered off, dried, and transferred to a crucible. This is then placed over a burner, the flame of which is turned up very gradually, whereupon the cadmium present as the oxide should show a uniform brown color.

Cadmium may be precipitated as the oxalate in alcoholic solution, washed with alcohol, decomposed with acid





and the excess of acid titrated with potassium permanganate.

A very accurate method for determining cadmium is the precipitation with microcosmic salt, and conversion to the pyrophosphate. The precipitation should take place in a volume of one hundred cubic centimeters and the solution should contain ten grams of ammonium chloride. If allowed to stand the cadmium ammonium phosphate settles out nicely. There must be, however, no excess of ammonia, no free acid, and almost exactly ten grams of the ammonium salt per hundred cubic centimeters of solution. The following table gives a sample of the results obtained when the above conditions were observed:

: : : : : : :	:	:	:	:	:
: Amt. taken :	:	:	:	:	:
: .6972 gms. :	:	:	:	:	:
: .6972 " :	:	:	:	:	:
: .6969 gms. :	:	:	:	:	:
: .6962 " :	:	:	:	:	:

When the cadmium can be obtained in solution as the sulphate, electrolysis is recommended as being not only the most convenient but by far the most accurate method for determination. The deposition requires some six or seven hours with a stationary anode, while according to Smith equally as good results may be obtained in eight to ten minutes by using a rotating anode.

It is proposed to make use of two methods in the present investigation. One of these was developed by Millar and takes advantage of the fact that the hydroxides of zinc, copper, and iron will not precipitate in a solution



which contains even a moderate amount of tartaric acid. After boiling for a short time, however, the cadmium comes down very nicely as a white, flocculent precipitate. Although this method is probably not used technically, it is well worth consideration.

The second method which it is proposed to use is the precipitation of the cadmium as the sulphide in a solution of potassium cyanide, or by using the inverse process suggested by Low, and mentioned previously in this paper. After filtering off and washing the precipitate in the usual manner it is to be dissolved in acid and the hydrogen sulphide which is evolved, absorbed in an excess of iodine. The amount of iodine used may then be determined by titration with thiosulphate.

The first analytical work done was the analyzing of several samples of zinc concentrate in order to get at the approximate relation which the amount of zinc bears to the amount of iron, lead, and copper. The method for decomposing the ore was as follows: Ten gram samples of the finely ground concentrate were treated with twenty-five cubic centimeters of concentrated nitric acid and ten of concentrated hydrochloric. The solution was evaporated down to a small volume and ten cubic centimeters of concentrated sulphuric acid added. The evaporation was then continued until dense white fumes of sulphur tri-oxide came off. A moderate amount of water was then added and the solution brought to a boil for a few seconds. After allowing the insoluble matter





to settle the supernatant liquid was decanted through a filter and the residue washed by decantation. The residue was once more treated with small amounts of acid and then finally thrown upon the filter and washed thoroughly. This gave the solution from which the cadmium was to be separated.

The results obtained from four samples were:

	#6	#7	#8	#9
Zinc	59.50	58.20	61.46	58.80
Iron	1.34	2.36	1.36	2.34
Lead	.75	.74	1.65	1.15

The amount of copper found in zinc blende being usually very small, it was not determined. In making up a test solution, however, a crystal of copper sulphate was always added in order to make the conditions as adverse and at the same time as typical as possible.

Using the results of the above analysis as a basis a test solution was prepared, two hundred and fifty cubic centimeters of which was calculated to correspond to a ten gram sample of a zinc concentrate of average composition. A series of samples taken from this solution was then run, the main purpose in view being to test the efficiency of a five per cent solution of sulphuric acid as a precipitating medium. A four and even a seven per cent solution were also tried, but it was quite evident that a five per cent solution gave the most consistent results. This was tried in a qualitative manner only, the rapidity of precipitation and the



filtering qualities of the precipitate being watched carefully. It was found that if the solution was allowed to stand for about an hour after precipitation the mixed sulphides would filter off in a satisfactory manner.

The same test solution containing a known amount of cadmium was next used, in order to attempt the separation by means of potassium hydroxide in a solution of tartaric acid. The exact method of procedure was as follows:- Two hundred and fifty cubic centimeter samples were diluted to four hundred and fifty, and the acidity brought up to five per cent by the addition of concentrated sulphuric acid. After running in hydrogen sulphide the solutions were allowed to stand two or three hours before filtering. The clear liquid was then decanted, the precipitate washed by decantation four or five times and then once or twice on the filter. The precipitate was returned to the original beaker, about twenty-five cubic centimeters of dilute hydrochloric acid were added, and the beaker heated. This dissolved all of the cadmium sulphide but left a part of the copper undissolved. After filtering, the solution thus obtained was treated with ten cubic centimeters of a saturated solution of tartaric acid, then with a solution of potassium hydroxide to alkalinity, and about ten cubic centimeters in excess. The solution was then boiled and within two minutes the cadmium precipitated very nicely. This precipitate was filtered off and washed several times, dissolved in acid, and reprecipitated with potassium hydroxide. It was thought that this procedure would decrease the amount





of alkalie occlusion. After washing this second precipitate of cadmium hydroxide very thoroughly it was dissolved in standard acid and the excess of the latter titrated with standard alkalie. The results which were obtained checked very nicely and gave a cadmium content not far from the theoretical value. Following are the results:-

No	Cadmium in Soln.	Cadmium found
1	.1030 gms.	.0980 gms.
2	.1040 "	.1040 "
3	.1172 "	.1074 "
4	.1172 "	.1070 "

The next work was also upon the separation by potassium hydroxide. This set of samples was run, however, to determine the difference which would be shown in the results if only one instead of two precipitations were made. The results were:-

No	Precipitations	Cd in Soln.	Cd found
1	2	.0529 gms.	.0501 gms.
2	2	.0527 "	.0507 "
3	1	.0359 "	.0450 "
4	1	.0275 "	.0315 "

While no attempt is made at criticising the above method it must be admitted that the procedure is rather long, that there is considerable danger of alkalie occlusion, and that even with experience it probably would not afford



an unusual degree of accuracy.

Before making application of Wohler's cyanide method, it was considered the best policy to make the precipitation in a five per cent solution of sulphuric acid as heretofore. The main advantage to be gained by this procedure is the elimination of all except a very small part of the large amount of zinc originally present.

As a first step a series of precipitates obtained from zinc concentrate by precipitation in a five per cent solution of sulphuric acid was analyzed for zinc, iron, and cadmium. It was thought that the results of this work would be a valuable criterion as to just what one would have to handle in separating the cadmium from the rest of the metallic sulphides. The average composition of the precipitates was found to be:-

:	:	:	:
Zinc	Iron	Cadmium	Copper
:	:	:	:
.03 gm.	.003 gm.	.02 gm.	Trace

As had been done previously a test solution, having about the composition shown in the table for each two hundred and fifty cubic centimeters, was then prepared. Different amounts of cadmium were added and the precipitation in a solution containing potassium cyanide was studied qualitatively.

To the first samples rather a large excess of potassium cyanide was added. When hydrogen sulphide was run in there was an immediate formation of a yellow, perfect





colloidal solution. This gradually became cloudy and within a minute or two there existed only a canary yellow precipitate. This persisted in passing through the filter even after allowing it to settle, or after heating on the steam bath.

In order to produce a more granular precipitate the effect of the addition of an electrolyte was next studied. The electrolyte first used was sodium chloride, and while it hastened precipitation and improved the quality of the precipitate, it did not produce the results desired. The effect of ammonium nitrate in both small and large quantities was then tried.

It having been determined that a large excess of potassium cyanide had a deleterious effect, it was the intention to use only a very slight excess in future work. The effect of precipitating at twenty-five and at fifty degrees was also studied at the same time. To this end four solutions were arranged as indicated in the diagram.

I	II	III	IV
2 gms. $\text{NH}_4\text{NO}_3$	40 gms. $\text{NH}_4\text{NO}_3$	2 gms. $\text{NH}_4\text{NO}_3$	40 gms. $\text{NH}_4\text{NO}_3$
25 deg.	25 deg.	50 deg.	50 deg.

Upon the addition of hydrogen sulphide to each of the solutions the first showed only an opacity, entirely unsatisfactory; the second gave a light yellow precipitate which showed itself to be granular; the third was unsatisfactory; and the fourth, after heating on the steam bath, yielded a precipitate of about the same quality as that obtained



from the second.

The results of this work would seem to show that the presence of a rather large quantity of some electrolyte, such as ammonium nitrate, is necessary, and that precipitation carried on in the cold gives as good results as that carried on at higher temperatures.

After obtaining a method which gave a satisfactory precipitate of cadmium sulphide the next problem was to find a rapid and accurate method for estimating the cadmium present. As already mentioned it was proposed to dissolve the cadmium sulphide in acid and absorb the hydrogen sulphide which was liberated in iodine. The amount of iodine added being known, the excess could then be titrated with thiosulphate. A trial of this method gave the following results:-

No	Cd. Present	Cd. Found
1	.085 gms.	.092 gms.
2	.085 "	.084 "
3	.1325 "	.1326 "
4	.1325 "	.1331 "

For the purpose of testing the entire method, ten gram samples of zinc concentrate were run as follows:- Three samples by repeated precipitation as the sulphide in acid solution; three by precipitation as the sulphide in a solution of potassium cyanide; and four according to the method suggested by Low. The cadmium in the first three samples was determined as the sulphate, that in the others by titration with iodine. The results showing comparative values





are given below:-

No.	Lab. No.	Method used	Cadmium found
1	9	Repeated Ppt.	.0365 gms.
2	9	" "	.0390 "
3	9	" "	.0290 "
4	9	Ppt'd in cyanide	.0406 gms.
5	9	" " "	.0397 "
6	9	" " "	.0400 "
7	9	Low's method	.0365 "
8	9	" "	.0359 "
9	2	" "	.01901 "
10	2	" "	.01918 "



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